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Underwater superoleophobic cellulose/electrospun PVDF–HFP membranes for efficient oil/water separation

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HIGHLIGHTS

- Modification of electrospun PVDF–HFP membrane by 3D cellulose penetration
- Hydrophobic membrane becomes superhydrophilic with enhanced mechanical behavior.
- Cellulose provides control over membrane pore size, porosity and wettability.
- Composite membrane is used for oil–water separation with high efficiency.

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ABSTRACT

Electrospun polyvinylidene fluoride-co-hexafluoropropylene (PVDF–HFP) nanofibers have been modified with cellulose regenerated from ionic liquid solution. Three-dimensional impregnation of cellulose provides greater control over porosity, pore size, wettability as well as the mechanical and thermal properties of the electrospun membrane. Formation of smaller pores with narrower pore size distribution is achieved as the fibers are coated with cellulose matrix. At 15 wt.% cellulose, the mechanical properties of electrospun PVDF–HFP are enhanced as the elastic modulus increases from 17 MPa to 54 MPa and the tensile strength also improves from 5.5 MPa to 8.6 MPa. The resulting membrane exhibits superhydrophilicity and underwater supoeroleophobicity and is successfully applied for selective separation of water from oil with efficiencies up to 99.98%.

1. Introduction

Wastewater transported to the surface with oil is known as produced water. Produced water accounts for the largest byproduct during oil and gas extraction [1]. It is a combination of seawater trapped in petroleum reservoirs as well as injected water and chemicals used during the extraction process [2]. Produced water can be of varying salinity and usually consists of oil, salts and other organic and inorganic matter [3]. Treatment of produced water by removal of oil and other contaminants is essential for minimizing adverse environmental impacts upon discharge or reuse. The U.S. Environmental Protection Agency (EPA) regulates produced water discharge at a maximum oil concentration of 29 ppm [2]. However, the high costs associated with treatment processes can lower the viability of oil production. Thus, the development of inexpensive methods to treat produced water remains an area of great interest for worldwide oil producers.

Current techniques for oil/water separation such as air flotation, chemical treatment and electrical processes are energy-intensive and require complicated machinery [4]. As such, membrane technology has gained popularity over the last few decades. Polymeric membranes with pores ranging from 0.1 to 10 μm have low pressure requirements and are thus promising for simple, low-cost and effective separation of oil–water mixtures. Most membranes used for oil/water separation rely on oil-absorbent and water-repellent materials. However, hydrophobic membranes are prone to fouling and pore clogging by oil droplets, and thus have limited reusability [5]. Recently, emphasis has been placed on materials with bio-inspired special wettability, i.e. superhydrophilicity and underwater superoleophobicity, which helps prevent such problems [4,6–12]. Membranes based on inorganic materials have also been used, but their viability is limited by their high costs. Techniques that allow control over pore size and wettability are highly desirable for membrane fabrication. Hydrophilicity of polymers has previously been improved by plasma treatment, surface graft copolymerization or hydrophilic coatings that use either synthetic polymers or inorganic materials [4,10,13–16]. However, as fossil fuel

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resources are running out, it is important to shift to functional materials that are based on natural, renewable and biodegradable resources.

Cellulose is the most abundant natural raw material in the world. Apart from being biodegradable and biocompatible, cellulose possesses excellent thermal and chemical stability. Cellulosic membranes have attracted interest in water treatment for years. Cellulose can also be modified into several different structures. Cellulose regenerated from ionic liquid: 1-allyl-3-methylimidaxolium chloride (AmimCl) constitutes a 3D hydrogen bonding network with increased functionality as compared to native cellulose [17]. However, cellulose processing in the past was largely limited due to lack of non-toxic direct solvents. The use of ionic liquids as non-derivatizing direct solvents for cellulose has facilitated cellulose processing and modification in the last decade [18]. Modification of native cellulose to more amorphous regenerated cellulose allows greater accessibility and is an important step for the fabrication of multifunctional composite materials.

Electrospinning is a low-cost and versatile technique to produce nonwoven nanofiber membranes with very high surface area to volume ratio, highly porous structures and tunable morphology. Electrospun nanofibers are particularly attractive as fillers for functional composites as they are continuous, possess high surface-to-volume ratio and are able to uniformly disperse through the matrix material [19]. Poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF–HFP) possesses good mechanical properties as well as high thermal and chemical stability. PVDF–HFP membranes have previously been applied to seawater desalination, batteries and solar cells [20–23]. However, the inherent hydrophobicity of PVDF–HFP membranes deters their long-term performance in filtration media as they show poor resistance to fouling by contaminants [14].

Chu et al. [24,25] previously fabricated thin film composite membranes using cellulose and chitin films regenerated from ionic liquid as the barrier layer with electrospun polyacrylonitrile (PAN) and polyethylene terephthalate (PET) as support. However, they did not allow the barrier layer to penetrate through the nanofibrous support and the properties of the nanofibers were not altered. In this work, cellulose regenerated from the ionic liquid 1-ethyl-3-methimidazolium acetate ([EMIM] Ac) is penetrated through the electrospun membrane three dimensionally. This novel method of coating nonwoven nanofibers with cellulose in ionic liquid has been used to control the porosity, hydrophilicity and mechanical behavior of electrospun PVDF–HFP membranes. Cellulose/electrospun PVDF–HFP membranes have been fabricated via electrospinning and a direct coating technique. Key membrane features including morphology, porosity, wettability as well as mechanical and thermal properties have been studied. The composite membrane is successfully used for separation of water from oil with high efficiency.

2. Materials and methods

2.1. Fabrication

Acetone, D-methylacetamide (DMA) and 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) (≥90%) were purchased from Sigma Aldrich. Microcrystalline cellulose, Avicel PH 101 (Mw: 160 kDa–560 kDa), was purchased from FMC Biopolymer. PVDF–HFP was obtained from Kynar Powerflex LBG. Silwick and Galwick were obtained from Porous Materials Inc. All materials were used as received.

PVDF–HFP was dissolved in a binary mixture of acetone and DMA with a weight ratio of 7:3. A clear solution of 10 wt.% PVDF–HFP was prepared with a magnetic stirrer at room temperature. A Nanon-01A setup (MECC, Japan) was used for electrospinning at room temperature with 60% relative humidity inside the chamber. The electrospinning setup consists of a needle and a rotating aluminum drum grounded target. The needle tip–collector distance was kept at 15 cm and a voltage of 24 kV was applied between the needle and drum. The PVDF–HFP solution was placed in a syringe with a needle of diameter 0.8 mm. A voltage of 25 kV was applied between the needle and rotating drum. The solution feed rate was kept at 1 ml/h. Electrospun PVDF–HFP nanofibers were collected on the rotating drum and dried in a conventional oven at 40 °C for 24 h. The electrospun membranes were hot-pressed for dimensional stability using a previously described procedure [20].

Microcrystalline cellulose (MCC) and ionic liquid [EMIM]Ac were vacuum dried for 24 h at 60 °C. A 5 wt.% solution of cellulose was then prepared by vigorously stirring cellulose into ionic liquid at 85 °C for 30 min. Cellulose–EMIM Ac solution was directly coated onto electrospun PVDF–HFP membranes. The cellulose solution was left to penetrate through the fibrous mat at room temperature for 3 h. The resulting transparent gel was then immersed in water overnight to remove EMIM Ac. It was then stirred in boiling water for 2 h and washed with deionized water multiple times. Conductivity tests were performed using an Accumet XL50 (Fisher Scientific) conductivity meter to ensure complete removal of ionic liquid. Cellulose/electrospun PVDF–HFP composite membranes were initially air-dried at 35 °C for 12 h and then vacuum dried at 60 °C for 6 h before characterization. The resulting membranes had a thickness of ~100 μm. A schematic of the fabrication process is shown in Fig. 1.

2.2. Characterization

2.2.1. Morphology

Morphology of electrospun PVDF–HFP and cellulose/electrospun PVDF–HFP was examined using field-enhanced scanning electron microscopy (FEI Quanta FEG 250, Netherland) under high vacuum. Samples were first coated with gold using a precision etching coating system (Gatan Model 682, Germany).

2.2.2. Pore size distribution

Pore size distribution (PSD) of the membranes was analyzed with PMI Capillary Flow Porometer (PMI, Ithaca, NY-USA). Samples were first wetted with Galwick (surface tension: 15.9 dynes/cm) and then the liquid was displaced from pores using a pressurized gas. The instrument determines pore size distribution and average pore size from the gas pressure needed to remove liquid from pores.

2.2.3. Porosity

Membrane porosity was measured by completely filling the pores of a membrane sample of known weight and dimensions with a highly wetting liquid of surface tension of 20.1 dynes/cm (Silwick®,

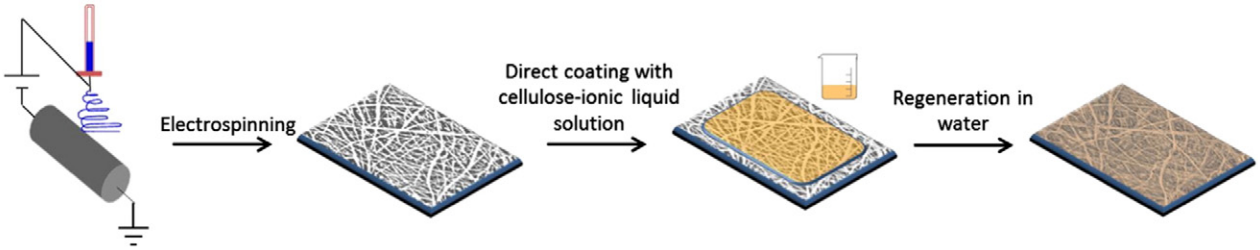

Fig. 1. Schematic representation showing fabrication process of cellulose/electrospun PVDF–HFP composite.